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PATENT

Attorney's Docket No. 1999DE119

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Box Patent Application
Assistant Commissioner for Patents
Washington, D.C. 20231

NEW UTILITY PATENT APPLICATION TRANSMITTAL

Sir:

Transmitted for filing on May 24, 2000 is the patent application of

Inventors: **Norbert WEFERLING**
Martin SICKEN
Hans-Peter SCHMITZ
Günter KOLBE

For: **PROCESS FOR PREPARING ALKYLPHOSPHONITE ESTERS**

1. This new application is for a(n)

   X Original (nonprovisional)
   _ Divisional
   _ Continuation
   _ Continuation-in-Part

2. Papers enclosed that are required for filing date under 37 CFR 1.53(b) (Regular)
   21 Pages of Specification and Claims (28 in number)
   1 Pages of Abstract
   0 N/A sheets of drawings

3. Additional papers enclosed:
   X Preliminary Amendment
   _ Information Disclosure Statement
   _ Form PTO-1449
   _ References Cited

4. Declaration or Oath:
   X Enclosed - EXECUTED BY INVENTORS
   _ Not Enclosed

5. An assignment of the invention to Clariant GmbH is attached. A separate "Assignment Recordation Form Cover Sheet" is also attached.

6. Certified copy of application from which priority is claimed is attached.

Country	Application No.	Filed
Federal Republic of Germany	199 23 615.1	May 25, 1999

7. Fee calculation

CLAIMS AS FILED					
Basic Filing Fee					**$690.00**
Number Filed		**NumberExtra**		**Rate**	
Total Claims:	28	Minus 20	=8	X $18.00	$ 144.00
Independent Claims:	1	Minus 3	=	X $78.00	
Multiple Dependent Claims (if any)				+$260.00	
TOTAL FEE DUE					**$834.00**

☐ Amendment canceling extra claims is enclosed.
☒ Amendment deleting multiple-dependencies is enclosed.
☐ Fee for extra claims is not being paid at this time.

Filing Fee Calculation $834.00

8. Fee Payment Being Made at this Time
☐ Not enclosed -- No filing fee is to be paid at this time.
x Enclosed
x Basic Filing Fee $834.00
x Assignment Recordation Fee 40.00

Total Fees Enclosed **$874.00**

9. Method of Payment

x The total filing fee calculated above is authorized to be charged to Deposit Account No. 03-2060 for which purpose a duplicate copy of this cover sheet is attached.

10. Authorization to charge additional fees/instructions as to overpayment

X The Commissioner is also authorized to credit any overpayments or charge any additional fees required under 37 CFR 1.16 (application filing fees) or 37 CFR 1.17 (application processing fees) during the prosecution of this application, including any related application claiming benefit hereof pursuant to 35 USC §120 (e.g., continuations, divisionals and/or CIPs under 37 CFR §1.53(b) and/or continuations, divisionals and/or CIPs under 37 CFR §1.53(b)) to maintain pendency hereof of any such related application.

Respectfully submitted,

Scott E. Hanf
Registration No. 38,906

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CERTIFICATION UNDER 37 CFR 1.10

Express Mail Mailing Label Number: EJ913191572US
Date of Mailing: May 24, 2000

I hereby certify that on the date indicated above, this new U.S. patent application and the papers indicated as enclosed therein, is being deposited with the United States Postal Service as "Express Mail Post Office to Addressee" addressed to: Assistant Commissioner for Patents, Box Patent Application, Washington, D.C. 20231, in accordance with 37 CFR 1.10.

Signature of Person Mailing the Application

Vicki L. Sgro
Typed Name of Person Mailing the Application

Attorney's Docket No. 1999DE119 Patent

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re U.S. patent of :
Norbert WEFERLING, et al. :
Serial No. to be assigned :
Filed: May 24, 2000 :
For: PROCESS FOR PREPARING :
ALKYLPHOSPHONITE ESTERS :

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
And Trademarks
Washington, DC 20231

Dear Sir:

Preliminary to the examination of the above-identified application, please enter the following preliminary amendment.

IN THE SPECIFICATION:

Page 1, line 1, insert "PROCESS FOR PREPARING ALKYLPHOSPHONITE ESTERS".

Page 1, line 2, insert --BACKGROUND OF THE INVENTION--.

Page 2, line 1, insert --SUMMARY OF THE INVENTION--.

Page 2, line 16, insert --DESCRIPTION OF THE PREFERRED EMBODIMENTS--.

Page 11, line 1, insert --EXAMPLES--.

Page 17, line 1, delete "Patent claims" and substitute therefor --CLAIMS--.

Page 22, before line 1, delete "Process for the preparation of alkylphosphonous acid esters".

Page 22, line 1, delete "Abstract" and substitute therefor --ABSTRACT OF THE DISCLOSURE--.

IN THE CLAIMS:

Please amend the claims as follows:

Claim 3, line 1, delete "or 2".

Claim 4, lines 1 and 2, delete "one or more of claims 1 to 3," and substitute therefor, --claim 1, --.

Claim 5, lines 1 and 2, delete "one or more of claims 1 to 3," and substitute therefor --claim 1,--.

Claim 6, lines 1 and 2, delete "one or more of claims 1 to 5," and substitute therefor --claim 1,--.

Claim 7, lines 1 and 2 , delete "one or more of claims 1 to 6," and substitute therefor --claim 1,--.

Claim 8, lines 1 and 2 , delete "one or more of claims 1 to 7," and substitute therefor --claim 1,--.

Claim 10, lines 1 and 2, delete "one or more of claims 1 to 9," and substitute therefor --claim 1,--.

Claim 11, lines 1 and 2, delete "one or more of claims 1 to 10," and substitute therefor --claim 1,--.

Claim 12, lines 1 and 2, delete "one or more of claims 1 to 11," and substitute therefor --claim 1,--.

Claim 13, lines 1 and 2, delete "one or more of claims 1 to 12," and substitute therefor --claim 1,--.

Claim 14, lines 1 and 2, delete "one or more of claims 1 to 12," and substitute therefor --claim 1,--.

Claim 15, lines 1 and 2, delete "one or more of claims 1 to 14," and substitute therefor --claim 1,--.

Claim 16, lines 1 and 2, delete "one or more of claims 1 to 15," and substitute therefor --claim 1,--.

Claim 17, lines 1 and 2, delete "one or more of claims 1 to 16," and substitute therefor --claim 1,--.

Claim 18, lines 1 and 2, delete "one or more of claims 1 to 17," and substitute therefor --claim 1,--.

Claim 19, lines 1 and 2, delete "one or more of claims 1 to 18," and substitute therefor --claim 1,--.

Claim 20, lines 1 and 2, delete "one or more of claims 1 to 19," and substitute therefor --claim 1,--.

Claim 21, lines 1 and 2, delete "one or more of claims 1 to 20," and substitute therefor --claim 1,--.

Claim 22, lines 1 and 2, delete "one or more of claims 1 to 21," and substitute therefor --claim 1,--.

Claim 23, line 1, delete "or 22".

Claim 24, line 2, delete "to 22".

Claim 25, line 2, delete "to 22".

Claim 26, line 2, delete "to 22".

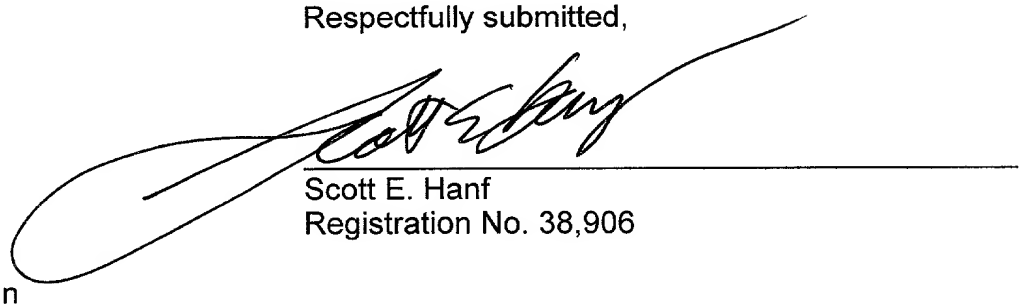
Claim 27, line 2, delete "to 22".

Claim 28, line 2, delete "to 22".

REMARKS

Entry of the above amendment is respectfully requested.

Respectfully submitted,



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The present invention relates to a process for the preparation of alkylphosphonous acid esters and to the use of the products prepared by this process.

Alkylphosphonous acid esters are valuable synthetic building blocks which can be employed, for example, for the preparation of crop protection agents and flame retardants.

The preparation of these compounds is technically complex and has hitherto been carried out, in the case of the particularly interesting esters of methylphosphonous acid, from the corresponding phosphonous acid dihalides by reaction with alcohols or by hydrolysis of the phosphonous acid dihalides to the phosphonous acids followed by esterification.

The phosphonous acid dihalides on which both processes are based, such as, for example, methyldichlorophosphine, which is extremely difficult to handle, have hitherto been prepared in a complex synthesis from phosphorus trihalides and alkyl halides in the presence of aluminum chloride (Houben-Weyl, Volume 12/1, p. 306). The reaction is highly exothermic and can only be controlled with difficulty in industry. In addition, various by-products are formed which, like some of the above-mentioned starting materials, are toxic, self-igniting and/or corrosive, i.e. are highly undesirable.

There is therefore a need for a process for the preparation of alkylphosphonous acid esters which can be carried out in a simple manner and in which uniform products are obtained in high yield. A process of this type should also be significantly superior to the processes known hitherto in economic and environmental terms.

The invention thus has the object of providing a process for the preparation of alkylphosphonous acid esters which avoids the above-mentioned disadvantages and, in particular, starts from easily handled, industrially available and readily controllable starting materials.

This object is achieved by a process of the type mentioned at the outset which comprises

a) reacting elemental yellow phosphorus with alkylating agents in the presence of a base to give a mixture which comprises, as principal constituents, the (metal) salts of alkylphosphonous, phosphorous and hypophosphorous acids,

b) esterifying the principal constituents of the mixture from a) to give an ester mixture,

c) isolating the ester of the alkylphosphonous acid from the ester mixture.

The process according to the invention has the considerable advantages over the processes known hitherto that it has a positive balance in the product distribution and at the same time avoids the phosphonous acid dihalide starting materials, which are regarded as undesired from various points of view.

The alkylating agents are preferably alkyl halides, dialkyl sulfates, trialkyl phosphates, dialkyl carbonates and/or formic acid ortho-esters.

The alkylating agents are particularly preferably methyl chloride, methyl bromide and/or dimethyl sulfate.

The bases are preferably hydroxides, carbonates, bicarbonates, amides, alkoxides and/or amine bases.

The reaction in step a) is preferably carried out in a two-phase system comprising aqueous alkali or alkaline-earth metal hydroxide or mixtures thereof and an organic solvent.

The organic solvents employed are preferably straight-chain or branched alkanes, alkyl-substituted aromatic solvents, water-immiscible or only partially water-miscible alcohols or ethers, alone or in combination with one another.

The organic solvent employed is particularly preferably toluene, alone or in combination with alcohols.

The reaction can, if desired, also be carried out in a non-aqueous system, for example by using solid sodium hydroxide or amines.

The reaction is preferably carried out in the presence of a phase-transfer catalyst.

The phase-transfer catalyst is preferably a tetraalkylphosphonium halide, triphenylalkylphosphonium halide or tetraorganylammonium halide.

The temperature during the reaction is preferably from -20 to +80°C.

The temperature is particularly preferably from 0 to 30°C.

The reaction is preferably carried out under a pressure of from 0 to 10 bar.

The process according to the invention is preferably carried out by suspending or dissolving the yellow phosphorus in a solvent or solvent mixture and then reacting it with an alkyl halide and a compound of the formula MOH or $M'(OH)_2$ or mixtures thereof, where M is an alkali metal and M' is an alkaline-earth metal.

The yellow phosphorus and the alkyl halide are preferably reacted with one another in a molar ratio of from 1:1 to 1:3, where the molar ratio of yellow phosphorus to the compound of the formula MOH or $M'(OH)_2$ is from 1:1 to 1:5.

The principal constituents of the mixture from a) are preferably esterified in step b) using a linear or branched alcohol of the general formula R-OH, where R is a linear or branched alkyl radical having 1 to 10 carbon atoms.

In another preferred embodiment of the process according to the invention, the principal constituents of the mixture from a) are converted into a mixture of alkylphosphonous, phosphorous and hypophosphorous acids using mineral acids, with the (metal) salts of the mineral acids simultaneously being precipitated, and the mixture of these acids subsequently being esterified.

The water formed during the esterification is preferably removed by azeotropic distillation.

In other words, the esterification of the phosphonous acid to the corresponding monoester can be achieved by reaction with relatively high-boiling alcohols with

removal of the resultant water by azeotropic distillation.

The precipitation of the metal salts, usually the alkali or alkaline-earth metal mineral salts, is preferably carried out here by replacement of the solvent water by the alcohol to be used in reaction step b).

The alkali or alkaline-earth metal mineral salt which has already precipitated is preferably filtered off before the esterification.

The alcohol is preferably n- or i-butanol, n-hexanol, ethylhexanol and/or amyl alcohol.

The mineral acid is preferably hydrochloric acid, sulfuric acid and/or phosphoric acid.

The mineral acid is particularly preferably hydrochloric acid.

The phosphines formed in small amounts during step a) are preferably removed by oxidation.

Hydrogen peroxide is preferably used as oxidant.

The ester of the alkylphosphonous acid is preferably removed by distillation in step c). The ester of the

alkylphosphonous acid is preferably n-butyl methylphosphonite, isobutyl methylphosphonite, n-hexyl methylphosphonite, 2-ethylhexyl methylphosphonite and/or amyl methylphosphonite.

The invention also relates to the use of the phosphonous acid esters prepared by the process according to the invention for the preparation of organophosphorus compounds.

The invention likewise relates to the use of the phosphonous acid esters prepared by the process according to the invention as precursors for chemical synthesis.

The invention also relates to the use of the phosphonous acid esters prepared by the process according to the invention for the preparation of phosphinic acids as starting materials for crop protection agents.

The invention also relates to the use of the phosphonous acid esters prepared by the process according to the invention as starting materials for the preparation of flame retardants.

The invention relates to the use of the phosphonous acid esters prepared by the process according to the invention as starting materials for the preparation of

flame retardants for thermoplastic polymers, such as polyethylene terephthalate, polybutylene terephthalate or polyamide.

The invention also relates to the use of the phosphonous acid esters prepared by the process according to the invention as starting materials for the preparation of flame retardants for thermosetting resins, such as unsaturated polyester resins, epoxy resins, polyurethanes or acrylates.

Surprisingly, it has been found that elemental yellow phosphorus can, after step a) of the process according to the invention, be reacted with alkylating agents in a two-phase system (organic solvent/base) and, if desired, in the presence of a (phase-transfer) catalyst under extremely mild conditions to give the (metal) salt of the corresponding alkylphosphonous acid RP(:O)HOH.

In addition, small amounts of dialkylphosphinic acids, trialkylphosphine oxide $R_3P(:O)$, dialkylphosphine oxide and unidentified phosphorus compounds may be formed; these can be removed from the product mixture in the usual manner. A further by-product formed is hydrogen, which can easily be separated off from the reaction mixture. The above-mentioned dialkylphosphinic acids can be separated off from the reaction mixture and employed or further processed elsewhere.

Surprisingly, neither phosphine (PH_3) nor alkylphosphines (RPH_2, R_2PH) are formed in significant amounts in the process according to the invention. Through the choice of suitable reaction conditions - such as the addition of small amounts of alcohols to the organic phase - the formation of all unidentified phosphorus-containing by-products is minimized to a surprisingly low content of a few mol% of the yellow phosphorus employed, in favor of the main product, the (metal) salts of alkylphosphonous acid.

The process according to the invention can be carried out, for example, by initially introducing the solvent together with the phase-transfer catalyst and, if necessary, warming the mixture to above the melting point of the yellow phosphorus, then adding the elemental (yellow) phosphorus, cooling the mixture to temperatures of, for example, from -10 to +30°C with vigorous stirring, and subsequently adding the alkylating agent.

The reaction is initiated by addition of the base. When the reaction is complete, the reaction system can be diluted, for example with water, and the readily volatile components (H_2, PH_3, RPH_2, R_2PH and excess alkylating agent, etc.) are subsequently removed.

This gives a base-containing/organic two-phase system, whose phases are separated. The contents from the phases are determined analytically.

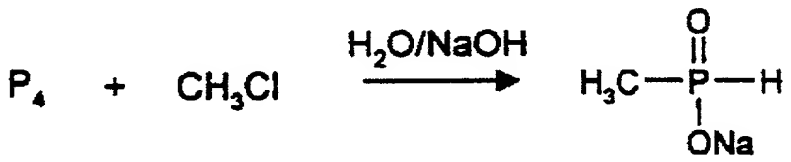
The reactants can also be combined in a different sequence, for example by introducing them continuously into a reactor (pressure tube, pressure reactor or cascade) in the above-defined molar ratio and removing them from the reactor again after a residence time of from 0.5 to 2 hours. The organic phase obtained after phase separation, which still contains the majority of any phase-transfer catalyst employed, is advantageously recycled.

The isolation of the pure alkylphosphonous acids from the mixture is carried out in a particularly simple manner via the corresponding esters, which, in contrast to the salts and acids of the alkylphosphonous acids, can be isolated from the mixture in a gentle manner by distillation. Although all other compounds present in the mixture are also partially esterified in steps b) and c) of the process according to the invention, they do not, however, form readily distillable products, and consequently the removal of the alkylphosphonous acid esters is achieved in surprisingly complete and pure form.

The invention is explained by the examples below:

Example 1: Ethylhexyl methylphosphonite

a1) Reaction of yellow phosphorus with alkyl chloride

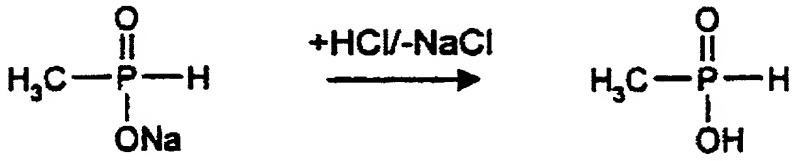


A solution of 26.1 g (0.05 mol) of tributylhexadecylphosphonium bromide in 1000 ml of toluene was introduced into a 5 l stainless-steel pressure reactor and pre-heated to 60°C. After 62 g (2 mol) of yellow phosphorus had been added, the mixture was cooled to -10°C with vigorous stirring, and 202 g (4 mol) of methyl chloride were then condensed in. 400 g of 50% aqueous sodium hydroxide solution were then metered in over the course of 2 hours, during which the temperature was held at -10°C. 400 g of water were added over the course of a further hour, the mixture was then stirred for a further hour and warmed to room temperature, and the reactor was subsequently decompressed via combustion. Two homogeneous liquid phases were obtained, which were separated and analyzed.

The aqueous phase (weight: 920 g) contained 65.6 mol% of methylphosphonous acid, 14.9 mol% of phosphorous acid, 13.7 mol% of hypophosphorous acid and 2.8 mol% of

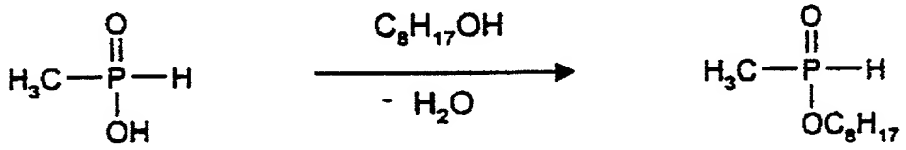
dimethylphosphinic acid in the form of their sodium salts and 3 mol% of dimethyldiphosphine.

a2) Conversion of the sodium salts into the acids/NaCl removal



In succession, 60 g of 5% aqueous hydrogen peroxide solution (in order to remove the dimethylphosphine), 240 g of 36% hydrochloric acid and 400 g of 2-ethylhexanol were added to the solution. After the water formed had been removed by distillation on a water separator, the precipitated sodium chloride was filtered off and washed with 100 g of 2-ethylhexanol. The ethylhexanol solutions now contained the compounds mentioned under a) as the free acids.

b) Esterification of methanephosphonous acid in the reaction mixture:



The ethylhexanol solutions from step a2) were combined and heated at about 120°C for 6 hours on a water separator under slightly reduced pressure.

c) Isolation of the ester:

The esterified reaction mixture was subsequently freed from excess ethylhexanol by distillation and subjected to a vacuum distillation. At a pressure of 0.3 mm and a head temperature of 75°C, 220 g of 2-ethylhexyl methanephosphonite passed over. The product was obtained in the form of a clear, colorless liquid in a purity of greater than 99%, corresponding to a yield of 58%, based on the yellow phosphorus employed. Analyses: 16.0% of phosphorus (theory: 16.2%); ^{31}P-NMR: doublet at 34 ppm (diastereomer pair)

Example 2: n-Hexyl methylphosphonite

910 g of an aqueous phase comprising 67.4 mol% of methylphosphonous acid, 14.6 mol% of phosphorous acid, 8.7 mol% of hypophosphorous acid and 3.8 mol% of dimethylphosphinic acid in the form of their sodium salts and 4 mol% of dimethyldiphosphine were obtained analogously to the process in step a1) of Example 1. In succesion, 60 g of 5% aqueous hydrogen peroxide solution, 240 g of 36% hydrochloric acid and 300 g of n-hexanol were added to the solution. After the water present had been removed by distillation on a water separator, the precipitated sodium chloride was filtered off and washed with 100 g of n-hexanol. The hexanol solutions were combined and heated at about 140°C for about 8 hours on a water separator. The

esterified reaction mixture was subsequently freed from excess hexanol by distillation and subjected to a vacuum distillation. At a pressure of 0.3 mm and a head temperature of 62°C, 199 g of n-hexyl methanephosphonite passed over.

The product was obtained in the form of a clear, colorless liquid in a purity of greater than 99%, corresponding to a yield of 61%, based on the yellow phosphorus employed. Analyses: 18.5% of phosphorus (theory: 18.9%); ^{31}P-NMR: singlet at 34 ppm.

Example 3: i-Butyl methylphosphonite

26.1 g (0.05 mol) of tributylhexadecylphosphonium bromide in 1000 ml of toluene were introduced into a 5 l stainless-steel pressure reactor and pre-heated to 60°C. After 62 g (2 mol) of yellow phosphorus had been added, the mixture was cooled to 5°C with vigorous stirring, and 202 g (4 mol) of methyl chloride were then condensed in. The mixture was then warmed to about 20°C, and 500 g of 40% aqueous sodium hydroxide solution were metered in at this temperature over the course of 2 hours. 300 g of water were added over the course of one hour, the mixture was then stirred for a further two hours, and the reactor was subsequently decompressed via combustion. Two homogeneous liquid

phases were obtained, which were separated and analyzed.

The aqueous phase (weight: 920 g) comprised 64.6 mol% of methylphosphonous acid, 14.4 mol% of phosphorous acid, 12.7 mol% of hypophosphorous acid and 3.3 mol% of dimethylphosphinic acid in the form of their sodium salts and 5 mol% of dimethyldiphosphine. In succesion, 60 g of 5% aqueous hydrogen peroxide solution, 240 g of 36% hydrochloric acid and 300 g of isobutanol were added to the solution. After the water present had been removed by distillation on a water separator, the precipitated sodium chloride was filtered off and washed with 100 g of i-butanol. The butanol solutions were combined and heated at from 115 to 125°C for about 12 hours on a water separator. The esterified reaction mixture was subsequently freed from excess butanol by distillation and subjected to a vacuum distillation. At a pressure of 0.5 mm and a head temperature of 42°C, 158 g of i-butyl methanephosphonite passed over.

The product was obtained in the form of a clear, colorless liquid in a purity of greater than 99%, corresponding to a yield of 58%, based on the yellow phosphorus employed. Analyses: 22.6% of phosphorus (theory: 22.8%); ^{31}P-NMR: singlet at 34 ppm.

Example 4: n-Butyl methylphosphonite

The reaction of yellow phosphorus with methyl chloride/40% NaOH was carried out analogously to Example 3. The work-up was carried out using n-butanol.

The combined butanol solutions were heated at from 115 to 125°C for about 14 hours on a water separator. The esterified reaction mixture was subsequently freed from excess butanol by distillation and subjected to a vacuum distillation. At a pressure of 0.5 mm and a head temperature of 42°C, 153 g of n-butyl methanephosphonite passed over.

The product was obtained in the form of a clear, colorless liquid in a purity of greater than 99%, corresponding to a yield of 56%, based on the yellow phosphorus employed. Analyses: 22.4% of phosphorus (theory: 22.8%); ^{31}P-NMR: singlet at 34 ppm.

Patent Claims

1. A process for the preparation of alkylphosphonous acid esters, which comprises

a) reacting elemental yellow phosphorus with alkylating agents in the presence of a base to give a mixture which comprises, as principal constituents, the (metal) salts of alkylphosphonous, phosphorous and hypophosphorous acids,

b) esterifying the principal constituents of the mixture from a) to give an ester mixture,

c) isolating the ester of the alkylphosphonous acid from the ester mixture.

2. A process as claimed in claim 1, wherein the alkylating agents are alkyl halides, dialkyl sulfates, trialkyl phosphates, dialkyl carbonates and/or formic acid ortho-esters.

3. A process as claimed in claim 1 or 2, wherein the alkylating agent employed is methyl chloride, methyl bromide and/or dimethyl sulfate.

4. A process as claimed in one or more of claims 1 to 3, wherein the bases are hydroxides, carbonates, bicarbonates, amides, alkoxides and/or amine bases.

5. A process as claimed in one or more of claims 1 to 3, wherein the reaction in step a) is carried out in a two-phase system comprising aqueous alkali or

alkaline-earth metal hydroxide or mixtures thereof and an organic solvent.

6. A process as claimed in one or more of claims 1 to 5, wherein the organic solvents employed are straight-chain or branched alkanes, alkyl-substituted aromatic solvents, water-immiscible or only partially water-miscible alcohols or ethers, alone or in combination with one another.

7. A process as claimed in one or more of claims 1 to 6, wherein the organic solvent employed is toluene, alone or in combination with alcohols.

8. A process as claimed in one or more of claims 1 to 7, wherein the reaction is carried out in the presence of a phase-transfer catalyst.

9. A process as claimed in claim 8, wherein the phase-transfer catalyst is a tetraalkylphosphonium halide, triphenylalkylphosphonium halide or tetraorganyl-ammonium halide.

10. A process as claimed in one or more of claims 1 to 9, wherein the temperature during the reaction with the yellow phosphorus is from -20 to +80°C.

11. A process as claimed in one or more of claims 1 to 10, wherein the temperature during the reaction with the yellow phosphorus is from 0 to 30°C.

12. A process as claimed in one or more of claims 1 to 11, wherein the reaction is carried out under a pressure of from 0 to 10 bar.

13. A process as claimed in one or more of claims 1 to 12, wherein the principal constituents of the mixture from a) are esterified in step b) using a linear or branched alcohol of the general formula R-OH, where R is a linear or branched alkyl radical having 1 to 10 carbon atoms.

14. A process as claimed in one or more of claims 1 to 12, wherein the principal constituents of the mixture from a) are reacted with mineral acids to give a mixture of alkylphosphonous, phosphorous and hypophosphorous acids and at the same time the (metal) salts of the mineral acids are precipitated, and the mixture of these acids is subsequently esterified.

15. A process as claimed in one or more of claims 1 to 14, wherein the water formed during the esterification is removed by azeotropic distillation.

16. A process as claimed in one or more of claims 1 to 15, wherein the alcohol is n- or i-butanol, n-hexanol, ethylhexanol and/or amyl alcohol.

17. A process as claimed in one or more of claims 1 to 16, wherein the mineral acid is hydrochloric acid, sulfuric acid and/or phosphoric acid.

18. A process as claimed in one or more of claims 1 to 17, wherein the mineral acid is hydrochloric acid.

19. A process as claimed in one or more of claims 1 to 18, wherein the phosphines formed in small amounts in step a) are removed by oxidation.

20. A process as claimed in one or more of claims 1 to 19, wherein hydrogen peroxide is employed for the oxidation.

21. A process as claimed in one or more of claims 1 to 20, wherein the ester of the alkylphosphonous acid is removed by distillation in step c).

22. A process as claimed in one or more of claims 1 to 21, wherein the ester of the alkylphosphonous acid is n-butyl methylphosphonite, isobutyl methylphosphonite, n-hexyl methylphosphonite, 2-ethylhexyl methylphosphonite and/or amyl methylphosphonite.

23. The use of an alkylphosphonous acid ester prepared by a process as claimed in claims 1 to 22 for the preparation of organophosphorus compounds and derivatives.

24. The use of an alkylphosphonous acid ester prepared by a process as claimed in claims 1 to 22 as a precursor for chemical synthesis.

25. The use of an alkylphosphonous acid ester prepared by a process as claimed in claims 1 to 22 for the

preparation of phosphinic acids as starting materials for crop protection agents.

26. The use of an alkylphosphonous acid ester prepared by a process as claimed in claims 1 to 22 for the preparation of flame retardants.

27. The use of an alkylphosphonous acid ester prepared by a process as claimed in claims 1 to 22 for the preparation of flame retardants for thermoplastic polymers, such as polyethylene terephthalate, polybutylene terephthalate or polyamide.

28. The use of an alkylphosphonous acid ester prepared by a process as claimed in claims 1 to 22 for the preparation of flame retardants for thermosetting resins, such as unsaturated polyester resins, epoxy resins, polyurethanes or acrylates.

Process for the preparation of alkylphosphonous acid esters

Abstract

The present invention relates to a process for the preparation of alkylphosphonous acid esters which comprises

a) reacting elemental yellow phosphorus with alkylating agents in the presence of a base to give a mixture which comprises, as principal constituents, the (metal) salts of alkylphosphonous, phosphorous and hypophosphorous acids,

b) esterifying the principal constituents of the mixture from a) to give an ester mixture,

c) isolating the ester of the alkylphosphonous acid from the ester mixture.

The invention likewise relates to the use of the alkylphosphonous acid esters prepared by this process as precursors for further syntheses, inter alia for the preparation of crop protection agents.

Case No. 1999DE119 - US

COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY

As below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below, I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

PROCESS FOR PREPARING ALKYLPHOSPHONITE ESTERS

the specification of which

[X] is attached hereto

[ ] was filed on , 19 as application Serial No. /

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, § 119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Applications(s) for which Priority is Claimed:

Federal Republic of Germany, 199 23 615.1 of May 25, 1999

And I hereby appoint
Miles B. Dearth, Reg. No. 35,115; Scott E. Hanf, Reg. No. 38,906; Susan Jackson, Reg. No. 41,302; Hesna J. Pfeiffer, Reg. 22,640
all of CLARIANT CORPORATION, address as indicated below, respectively and individually, as my attorneys and/or agents, with full power of substitution, to prosecute this application, and transact all business in the Patent and Trademark Office connected therewith.

Please address all communications to Clariant Corporation, 4331 Chesapeake Drive, Charlotte, North Carolina 28216, whose Facsimile number is 704/395-6727.

Case No. 1998DE119 -US

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Signed: at Hürth, Federal Republic of Germany, this 2nd day of May, 2000

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